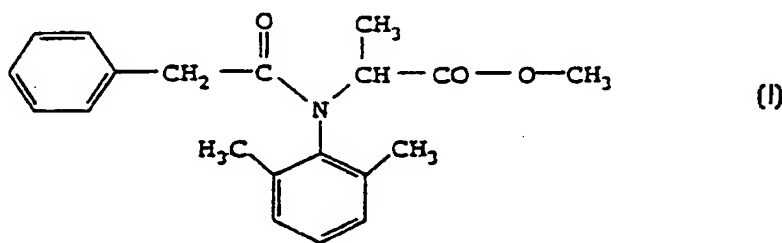




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N		A2	(11) International Publication Number: WO 98/26654
			(43) International Publication Date: 25 June 1998 (25.06.98)
(21) International Application Number: PCT/EP97/06968		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 6 December 1997 (06.12.97)		<p>Published Without international search report and to be republished upon receipt of that report.</p>	
(30) Priority Data: MI96A002660 19 December 1996 (19.12.96) IT MI97A001198 22 May 1997 (22.05.97) IT			
(71) Applicant (for all designated States except US): ISAGRO S.P.A. [IT/IT]; Via Felice Casati, 20, I-20124 Milano (IT).			
(72) Inventors; and (75) Inventors/Applicants (for US only): PALLA, Ottorino [IT/IT]; Via Goldoni, 7, I-26013 Crema (IT). MIRENNA, Luigi [IT/IT]; Via Gamboloita, 4, I-20139 Milano (IT). COLOMBO, Laura [IT/IT]; Via Bocconi, 60, I-20090 Lodi (IT). ZINI, Guido [IT/IT]; Viale Giulio Cesare, 24, I-28100 Novara (IT). FILIPPINI, Lucio [IT/IT]; Via Morandi, 13/A, I-20097 San Donato Milanese (IT). ZANARDI, Giampaolo [IT/IT]; Viale Roma, 19, I-28100 Novara (IT).			
(74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanò & Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121 Milano (IT).			

(54) Title: FUNGICIDAL COMPOSITIONS BASED ON (N-PHENYLACETYL-N-2,6-XYLYL)METHYL ALANINATE



(57) Abstract

Fungicidal compositions comprising: (a) the compound corresponding to (N-phenylacetyl-N-xylyl)methyl alaninate having formula (I), wherein more than 50 % of the compound with formula (I) consists of the laevorotatory enantiomorph; (b) one or more known fungicides. Among known fungicides, Mancozeb, Fosetil, Cymoxanil, Propamocarb, Chlorothalonil, salts of copper (I) or copper (II), etc., can be mentioned. The above compositions can be used in the agricultural field for controlling fungine diseases which seriously damage agricultural crops.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FUNGICIDAL COMPOSITIONS BASED ON (N-PHENYLACETYL-N-2,6-XYLYL)METHYL ALANINATE.

The present invention relates to fungicidal compositions based on (N-phenylacetyl-N-2,6-xylyl)methyl alaninate.

More specifically, the present invention relates to fungicidal compositions comprising the compound corresponding to (N-phenylacetyl-N-2,6xylyl)methyl alaninate, in which more than 50% of said compound consists of the laevorotatory enantiomorph, and one or more known fungicides and their use in the agricultural field for controlling fungine disease which seriously damage agricultural crops.

Many of the compounds which are used for controlling phytopathogen fungi in agrarian practice have at least one asymmetrical centre. In particular, when these compounds have only one asymmetrical centre, or chiral centre, the two enantiomorphs can have a different fungicidal activity.

More specifically, when only one of the enantiomorphs has a significant biological activity, it is possible for the same fungicidal effect to be obtained using the more efficient enantiomorph at a dosage which is half that of the raceme. Obviously when both enantiomorphs have a comparable biological activity, the reductions in the expected applicative dosages should in any case be less than 50% with respect to those of the raceme.

10 Most fungicidal compounds containing at least one chiral centre are normally sold as a racemic mixture as it is difficult to compensate the higher cost relating to the production of the enantiomorph in its pure form, with additional commercial advantages.

15 The necessity of improving the environmental impact has recently led to a re-evaluation of the use of single enantiomorphs to obtain at least partial reductions in the dosages used, thus diminishing the quantity of xenogene substances dispersed in the environment and improving the environmental impact of phytoiatric treatment.

In addition, it is particularly advantageous if products with a fungicidal activity can be easily degraded by the vegetable host at the end of the period for which the fungicidal activity is required, so as to

25

guarantee the minimum quantity of residual active principle.

The reduction in residues of main principle in vegetables when they are picked, is in fact linked to potential risk for possible consumers of the agricultural product: the smaller the quantity of residual active principle, the lower the risk will be for the consumer.

The compound (N-phenylacetyl-N-2,6-xylyl)-DL-methyl alaninate, also known under the trade-name of Benalaxyl, is particularly efficient in the control of diseases caused by Oomycetes. Oomycetes are responsible for many diseases of economically important crops such as, for example, grapes, potatoes, tomatoes and tobacco. This fungicide is described in U.S. patents 4.291.049 and 4.425.357.

Benalaxyl has one asymmetrical centre and consists of an equimolecular mixture of the two enantiomorphs. When prepared according to the methods described in the two U.S. patents cited above, Benalaxyl is obtained as a racemic mixture in which the enantiomorphs are present in equimolecular quantities.

"Pesticide Science" (1985), Vol. 16, pages 277-286, on the other hand also describes the preparation of the laevorotatory enantiomorph, corresponding to

(N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate and shows its greater activity with respect to both the dextrorotatory enantiomorph corresponding to (N-phenylacetyl-N-2,6-xylyl)-L-methyl alaninate and the raceme,
5 corresponding to (N-phenylacetyl-N-2,6-xylyl)-DL-methyl alaninate. This greater activity has been observed by both experimenting the laevorotatory enantiomorph in tests in vitro, and by applying it on infected plants or on plants infested after its application, and also by
10 applying it to the earth or plant seed, to control the pathogenes present in the soil.

Racemic Benalaxyl is degraded with a different rate depending on the type of vegetable and portion to which it is applied.

15 For example, the degradation rate of racemic Benalaxyl in hops makes the use of this product unsuitable as an antifungal agent, to the detriment of its distinct fungicidal efficiency: in fact, after two weeks following treatment, the residual levels of
20 active principle are still high.

Together with its good preventive activity, Benalaxyl also has considerable curative efficiency: it is in fact capable of blocking infections already in development consequently allowing intervention after
25 infection. In agrarian practice it is customary to

intervene within 72 hours of a possible infection such as, for example, rainfall or abundant night-dew.

Literature of the known art specifies that the MIC (minimum concentration of active principle necessary for inhibiting the development of disease) of the laevorotatory enantiomorph of Benalaxyl, when applied on the leaves of vines cultivated in a vase and infected 24 hours earlier with spores of Plasmopara viticola, is 5 mg/l, the MIC of the dextrorotatory enantiomorph is 100 mg/l and the MIC of the raceme is 10 mg/l.

The Applicant has now surprisingly found that the laevorotatory enantiomorph of Benalaxyl, corresponding to (N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate applied to leaves combined with one or more fungicides normally used for controlling phytopathogenic Oomycetes of economically important crops, has a higher synergetic activity than that possibly obtained with the racemic product used in a double dosage, consequently containing the same quantity of laevorotatory enantiomorph. This allows the production of more effective fungicidal compositions, having an improved environmental impact with respect to those obtained using racemic Benalaxyl.

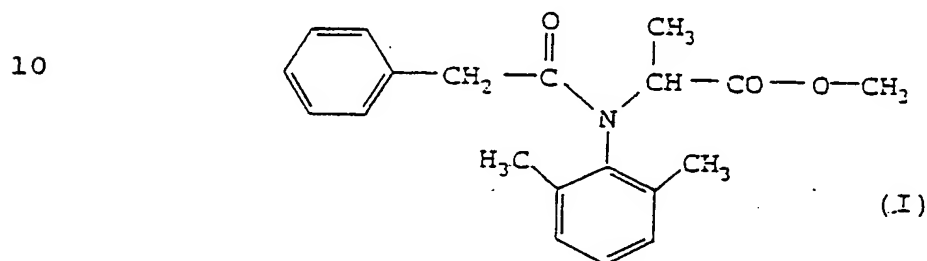
The above fungicidal compositions can be used in both curative and preventive applications, i.e. at

6

regular intervals. In treatment at regular intervals, its curative property is still important to fight infections which have possibly arisen during the last period of the interval of treatment.

5 The present invention therefore relates to fungicidal compositions comprising:

(a) the compound corresponding to (N-phenylacetyl-N-2,6-xylyl)methyl alaninate having formula (I):

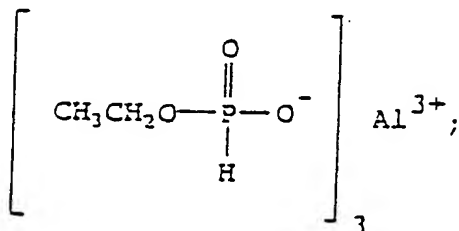


15 wherein more than 50% of said compound having formula (I) consists of the laevorotatory enantiomorph;

(b) one or more fungicides selected from:

(1) Cymoxanil corresponding to 1-(2-cyano-2-methoxyiminoacetyl)-3-ethyl-urea;

20 (2) Fosetyl having the formula:



25 (3) Metalaxyl corresponding to methyl-N-(2-metho-

xyacetyl)-N-2,6-xylyl-DL-alaninate;

(4) Oxadixyl corresponding to 2-methoxy-N-(2-oxo-1,3-oxazolidin-3-yl)--acet-2'-6'--xylidine;

5 (5) Ofurace corresponding to DL-3-[N-chloroacetyl-N-(2,6-dimethylphenyl)-amino]- γ -butyrolactone;

(6) Fluazinam corresponding to 3-chloro-N-[3-chloro--2,6-dinitro-4--(trifluoromethyl)-phenyl]-5-trifluoromethyl-2-pyridinamine;

10 (7) (E)-2-[2-([6--(2-cyanophenoxy)--pyrimidin-4-yloxy]-phenyl-3-methyl methoxyacrylate;

(8) (E)-methoxyimino- α -o-tolyloxy)-o-tolyl]-methyl acetate;

15 (9) N-methyl-(E)-methoxyimino-[2-(2,5-dimethylphenoxy)methyl)-phenyl] acetamide;

(10) N-methyl-(E)-methoxyimino-[2-phenoxyphenyl]acetamide;

20 (11) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-chloro-phenyl)-ethyl]-amino]-carbonyl]-propyl]-carbamate;

(12) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-methyl-phenyl)-ethyl]-amino]-carbonyl]-propyl]-carbamate;

25 (13) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-ethyl-phenyl)-ethyl]-amino]-carbonyl]-pro-

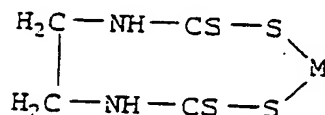
pyl]-carbamate;

(14) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-methoxyphenyl)-ethyl]-amino]-carbonyl]--propyl]--carbamate;

5 (15) O-(phenyl)--N--[2-methyl-1-[[[1-(4-methoxyphenyl)-ethyl]-amino]-carbonyl]--propyl]--carbamate;

(16) compounds belonging to the group of dithiocarbamates having the general formula:

10

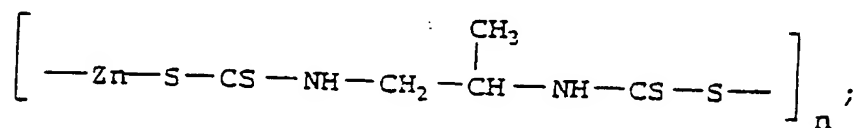


wherein M represents manganese or zinc;

(17) Thiram corresponding to bis-(dimethylthiocarbamoyl)-disulfide;

15

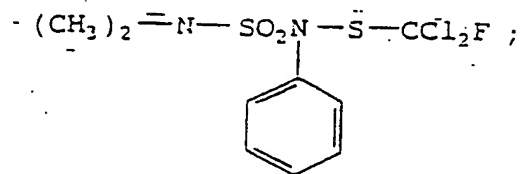
(18) Propineb having the formula:



(19) Anilazine corresponding to N-(4,6-dichloro-1,3,5-triazin-2-yl)-aniline;

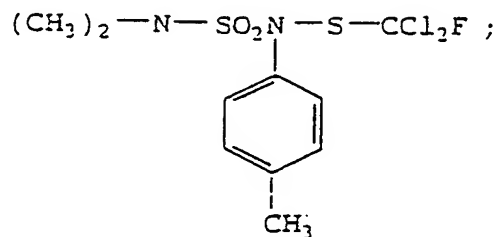
20

(20) Dichlofluanid having the formula:



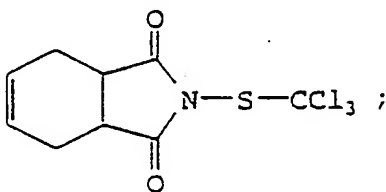
9

(21) Tolyfluanid having the formula:



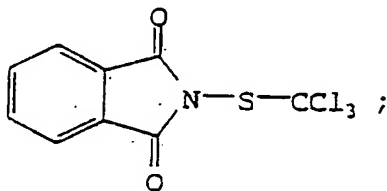
5

(22) Captan having the formula:



10

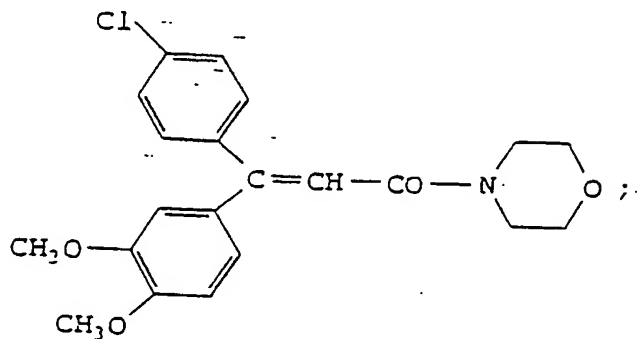
(23) Folpet having the formula:



(24) Chlorothalonil corresponding to 1,3-di-cyano-
2,4,5,6-tetrachlorobenzene;

15

(25) Dimethomorph having the formula:



20

(26) Flumetover corresponding to N,N-diethylamide
of 4-trifluoromethyl-6-(3,4-dimethoxyphenyl)-
benzoic acid;

25

- (27) Dithianon corresponding to 5,10-dihydro-5,10-dioxonaphthol-[2,3-b]-1,4-dithin-2,3-dicarbo-
nitrile;
- 5 (28) Tetraconazole corresponding to 1-(1H-1,2,4-triazol-1-yl)-2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy)-propane;
- (29) Propiconazole corresponding to 1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole;
- 10 (30) Triadimefon corresponding to 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butanone;
- (31) Triadimenol corresponding to 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-
15 butan-2-ol;
- (32) Bitertanol corresponding to 1-(diphenyl-4-yloxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-ol;
- (33) Etridiazole corresponding to ethyl 3-trichloromethyl-1,2,4-thiadiazolyl ether;
- 20 (34) Pencycuron corresponding to 1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea;
- (35) Hymexanol corresponding to 5-methylisoxazol-3-ol;
- 25 (36) Protiocarb corresponding to S-ethyl-(3-di-

//

methylaminopropyl)-thiocarbamate;

(37) Propamocarb corresponding to propyl 3-(dimethylamino)-propylcarbamate;

(38) salts of copper (I) or copper (II);

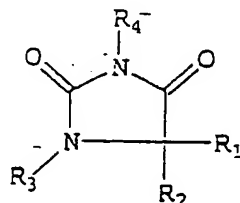
5 (39) Andoprim corresponding to 2-p-methoxy-aniline-4,6-dimethyl-pyrimidine;

(40) Famoxadone or DPX-JE874 corresponding to 5-methyl-5-(4-phenoxyphenyl)-3-(phenylamino)-oxazolidin-2,4-dione;

10 (41) 4-methyl-4-phenyl-1-(phenylamino)-2-methylthio-imidazolidin-5-one;

(42) pyrimidinic compounds such as, for example, cyprodinil, mepanipyrim, pyrethanil;

(43) compounds having the following general formula:



wherein:

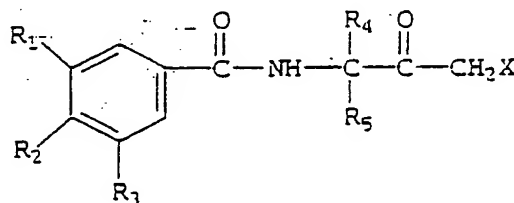
20 - R₁ and R₂, the same or different, represent a hydrogen atom; or a C₁-C₃ alkyl group; or, R₁ and R₂ together with the hydantoinic ring to which they are attached, represent a C₃-C₇ saturated spiro ring;

25 - R₃ and R₄, different from each other, repre-

/2

sent a C₁-C₃ alkyl group; a phenyl group, said phenyl group optionally substituted with a halogen atom, with a nitro group, with a C₁-C₃ alkoxyl group, or with a C₁-C₃ haloalkyl group; or a 3-iodo-propinyl group;

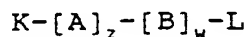
(44) compounds having the following general formula:



wherein:

- R₁ and R₃, the same or different, represent a halogen atom; or a C₁-C₄ alkyl group;
- R₂ represents a C₁-C₄ alkyl group; a C₂-C₄ alkenyl group; a C₂-C₆ alkynyl group; a C₁-C₄ alkoxyl group; a cyano group;
- R₄ and R₅, the same or different, represent a halogen atom; or a C₁-C₄ alkyl group; on the condition that, at least one between R₄ and R₅, is a C₂-C₄ alkyl group;
- X represents a halogen atom; a thiocyno group; an isothiocyno group;

(45) oligopeptidic compounds having the general formula:

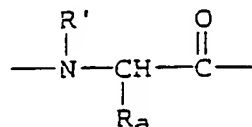


13

wherein:

- z and w, the same or different, are 1 or 2;
- A represents an aminoacidic portion having the general formula:

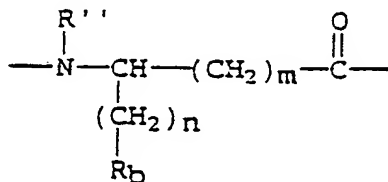
5



wherein:

- R_a represents a linear or branched $\text{C}_3\text{-C}_4$ alkyl group; or a $\text{C}_3\text{-C}_4$ cycloalkyl group;
- 10 - R' represents a hydrogen atom; a $\text{C}_1\text{-C}_3$ alkyl group; or, together with R_a it forms a linear or branched $\text{C}_3\text{-C}_5$ alkylene chain;
- B represents an aminoacidic portion having the general formula:

15

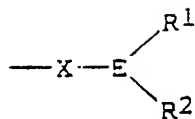


wherein:

- R_b represents a phenyl group or an aromatic heterocyclic group, said phenyl and heterocyclic groups, also optionally substituted;
- 20 - m and n, the same or different, are 0 or 1;
- R'' represents a hydrogen atom; or a $\text{C}_1\text{-C}_3$ alkyl group;
- 25 - L represents a group having the general

14

formula:



wherein:

- 5 - E represents a linear or branched C₁-C₈ alkyl-
ene chain; a linear or branched C₂-C₈ ω-oxal-
kyl chain; or a direct bond;
- 10 - R¹ represents a hydrogen atom; a C₃-C₆ cyclo-
alkyl group; a phenyl group or an aromatic
heterocyclic group, said phenyl and heterocy-
clic groups also optionally substituted;
- 15 - R² represents a hydrogen atom; a linear or
branched C₂-C₆ carboxyalkyl group; a linear,
branched or cyclic C₂-C₆ carbamoyl group; or
a cyano group;
- 20 - X represents an -O- group; an -N(R³)- group;
or an -N(R⁴)-O- group; wherein:
- R³ represents a hydrogen atom; a C₁-C₃
alkyl or alkoxyl group; or, together
with R₁, it represents a direct bond or
a linear or branched C₂-C₄ alkylene
chain;
- 25 - R⁴ represents a hydrogen atom; a C₁-C₃
alkyl group; or, together with R₁, it
represents a direct bond;

- K represents a hydrogen atom; a linear or branched C₁-C₄ alkyl group; or a protective group having general formula:



- Y represents an oxygen atom; or a direct bond;
- M represents a linear, branched or cyclic C₁-C₈ alkylene chain; or a direct bond;
- 10
- R⁵ represents a hydrogen atom; a phenyl group optionally substituted; a linear, branched or cyclic C₂-C₆ carbamoyl group; a linear, branched or cyclic C₁-C₆ carboalkoxyl group; or a cyano group;
- 15
- R⁶ represents a hydrogen atom; a C₁-C₃ alkoxyl group; an acetate group; or an acetamidic group;

20 (46) methylbenzothiadiazole-7-thiocarboxylate.

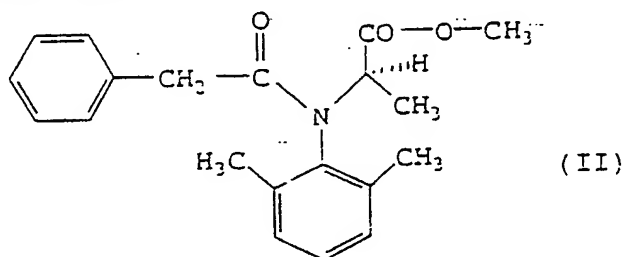
In the compositions of the present invention, the compound having general formula (I) preferably contains more than 90% of the laevorotatory enantiomorph, even more preferably at least 95% of the laevorotatory enantiomorph. Compositions in which the compound having

25

16

formula (I) contains at least 99% of the laevorotatory enantiomorph are even more preferred.

The laevorotatory enantiomorph corresponding to (N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate, has
5 the following formula (II):



10 The asymmetrical carbon present in the compound having formula (II) has the absolute configuration defined in said formula (II); this configuration can be described as D-shaped, according to the actual terminology of aminoacids, or R-shaped according to the
15 classification introduced by Cahn, Ingold and Prelog.

The improved environmental impact of the fungicidal compositions of the present invention is due to the fact that the compound having formula (I) in which more than 50% of said compound consists of the laevorotatory
20 enantiomorph, has a lower residual level of active principle in crops treated when the fungicidal activity is completed (as already mentioned above, racemic Benalaxyl on the other hand has even higher residual levels of active principle after two weeks following
25 treatment). The laevorotatory enantiomorph is therefore

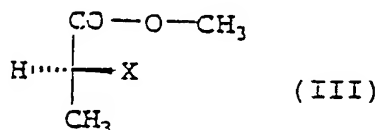
17

degraded more rapidly with respect to racemic Benalaxyl.

The compound having formula (I) can be conveniently prepared by various processes.

5 One process for the preparation of the compound having formula (I) comprises:

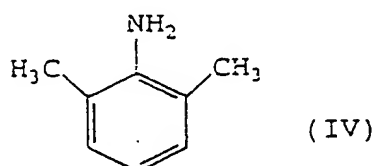
(a) reacting methyl ester having general formula (III):



10

having an S-type asymmetrical carbon and wherein X represents a halogen atom such as chlorine, fluorine, bromine or iodine; or X represents an activated ester such as a paratoluenesulfonate, a mesilate or triflate; with an xylydine having formula (IV):

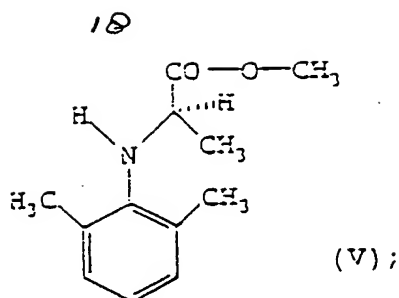
15



in the presence of or without an inert organic solvent or a mixture of inert organic solvents, at a temperature ranging from 60°C to the boiling point of the solvent system selected, in the presence of or without an organic or inorganic base, obtaining N-xylyl-D-methyl alaninate having formula (V):

20

25



5 (b) acylating the N-xylyl-D-methyl alaninate having formula (V) obtained in step (a), with a derivative of phenylacetic acid such as, for example, acyl chloride; or with a mixed anhydride obtained by reaction of the salt of phenylacetic acid with
10 an acyl chloride such as, for example, pivaloyl chloride; or with an alkyl chloroformate such as, for example, isobutyl chloroformate; in the presence of an inert organic solvent or a mixture of inert organic solvents, at a temperature
15 ranging from -30°C to +120°C, in the presence of or without an organic or inorganic base, obtaining the compound having formula (I).

Examples of inert organic solvents which can be used in step (a) of the above process are: aromatic
20 solvents such as, for example, toluene, xylene; protic solvents such as, for example, ethanol, propanol, butanol, octanol; dipolar aprotic solvents such as, for example, N,N-dimethyl-formamide, N-methylpyrrolidone, dimethylsulfoxide; or their mixtures.

25 Examples of organic bases which can be used in

19

step (a) of the above process are tertiary amines such as, for example, triethylamine.

Examples of inorganic bases which can be used in step (a) of the above process are alkaline carbonates
5 or hydrogencarbonates such as, for example, sodium hydrogencarbonate and potassium carbonate.

The use of the above bases must, however, be carefully effected in order to avoid racemizations of the asymmetrical carbon.

10 Examples of inert organic solvents which can be used in step (b) of the above process are: esters such as, for example, ethyl acetate; chlorinated solvents such as, for example, methylene chloride, dichloroethane; aromatic solvents such as, for example, toluene,
15 xylene; hydrocarbons such as, for example, hexane, petroleum ether; or their mixtures.

Examples of organic bases which can be used in step (b) of the above process are tertiary amines such as, for example, triethylamine, N-methylmorpholine; or
20 heterocyclic amines such as, for example, pyridine.

Examples of inorganic bases which can be used in step (b) of the above process are alkaline carbonates such as, for example, sodium carbonate.

The Applicant has however surprisingly found, and
25 this is therefore a further object of the present

20

invention, that step (b) of the above process is conveniently carried out in the presence of an aromatic solvent (for example, toluene, etc.), or a halogenated solvent (for example, dichloromethane, dichloroethane, etc.) or an ester solvent (for example, ethyl acetate), at a temperature ranging from -20°C to +40°C, preferably between -5°C and +25°C, in the presence of an inorganic base (for example, sodium bicarbonate, etc.) or an organic base (for example, triethylamine, pyridine, etc.). Operating under these conditions, products are obtained with a higher ratio D/S isomers than that obtained operating according to the known method described in "Pesticide Science (1985)", Vol. 16, pages 277-286, which consists in reacting N-xylyl-D-methyl alaninate having formula (V) with the chloride of phenylacetic acid in the presence of toluene, at a temperature of 80°C, without bases.

In fact operating according to this method, products are obtained with a satisfactory ratio D/S isomers only after repeated crystallizations which cause considerable reductions in the yield.

The methyl ester having general formula (III), can be conveniently prepared starting from aminoacid alanine, by diazotization of the amine group in the presence of a halide ion as described, for example, in

21

"Methoden der Organischen Chemie - Band V/4 - Halogen Verbindungen" (1960), page 458, obtaining the corresponding halogenated acid having general formula (VI):



wherein X has the same meaning described above, which is subsequently esterified to obtain methyl ester having general formula (III) according to any of the usual known methods in organic practice.

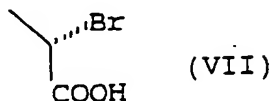
When X, in the methyl ester having general formula (III), represents an activated ester, said methyl ester having general formula (III), is conveniently obtained from methyl lactate, a compound which is commercially available at a low cost, by reaction with a suitable derivative of methanesulfonic, paratoluenesulfonic, trifluoromethanesulfonic acids such as, for example, a chloride or an anhydride, in the presence of or without an organic base such as, for example, triethylamine, N-methylmorpholine, pyridine, or an inorganic base such as, for example, sodium bicarbonate.

The xylidine having formula (IV) is a compound which is commercially available.

Alternatively, the above process can be modified by carrying out the condensation of xylidine having

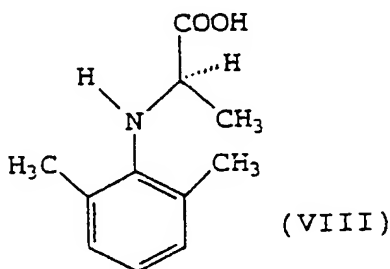
22

formula (IV), described above, with an acid such as, for example, S-bromo propionic acid having formula (VII):



5

to obtain N-aryl-D-aminoacid having formula (VIII):



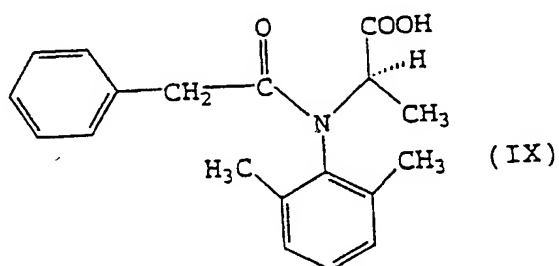
10

which is subsequently esterified with methanol (CH_3OH) in an acid environment by the addition, for example, of hydrochloric acid or sulfuric acid, operating at a temperature ranging from 20°C to the boiling point of the solution, obtaining N-xylyl-D-methyl alaninate having formula (V) described above. Or, the N-aryl-aminoacid having formula (VIII) can be acylated with the chloride of phenylacetic acid, operating under the same conditions described in step (b) of the process described above for the acylation of N-xylyl-D-methyl alaninate having formula (V), or operating in an aqueous environment made basic with inorganic bases such as, for example, sodium bicarbonate or sodium hydroxide, possibly in the presence of an organic

25

cosolvent such as, for example, methylene chloride, ethyl acetate, or tetrahydrofuran, operating at a temperature ranging from 0°C to 20°C, obtaining the acid having formula (IX):

5



10 which is subsequently transformed into (N-phenylacetyl-N-2,6-xylyl)-methyl alaninate having formula (I), by esterification with methanol, in the presence of acids such as, for example, hydrochloric acid or sulfuric acid, operating at a temperature ranging from 20°C to
15 the boiling point of the solution.

S-bromo propionic acid having formula (VII) is a product which is commercially available.

A further process which can be used for the preparation of the compound having formula (I) consists
20 in partially hydrolyzing the compound (N-phenyl-acetyl-N-2,6-xylyl)-DL-methyl alaninate (in racemic form), in the presence of enzymes. Depending on the type of enzyme used, the compound having formula (I) can be obtained in its acid form which can be subsequently
25 transformed into the desired compound having formula

(I) operating according to the usual methods described in literature. Or, the laevorotatory compound having formula (I) contained in the racemic product is preserved, whereas the dextrorotatory compound having
5 formula (I) is hydrolyzed to acid.

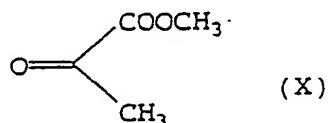
The above hydrolysis reactions can be carried out both in the presence of inert organic solvents such as, for example, chloroform, ethyl acetate, dioxane, and in water maintained at a constant pH by the addition of
10 suitable quantities of inorganic salts to obtain buffer systems. The temperature is maintained at -10°C to $+40^{\circ}\text{C}$, care being taken not to select temperatures which cause denaturation of the enzymes used. The above enzymatic-type reaction can also be carried out on
15 N-xylyl-DL-methyl alaninate to obtain N-xylyl-D-methyl alaninate having formula (V), which is subsequently transformed into the compound having formula (I) operating as described in step (b) of the process described above.

20 The acid or dextrorotatory ester, obtained with the method described above, can be subsequently racemized in basic environments and then subjected to further enzymatic treatment.

Another process which can be used for the preparation
25 tion of the compound having formula (I) consists in

salifying N-xylyl-DL-methyl alaninate with an enantio-
merically pure acid such as, for example, tartaric acid
or camphorsulfonic acid. The salt thus obtained can
give, by fractionated crystallization, the salt corre-
5 sponding to N-xylyl-D-methyl alaninate in an enantio-
merically pure or enriched form. The salification
reaction takes place in the presence of solvents such
as, for example, halogenated solvents (methylene
chloride, etc.), aliphatic esters (ethyl acetate,
10 etc.), aromatic solvents (toluene, etc.), or their
mixtures. Further possible recrystallizations followed
by treatment of the salified form with basic aqueous
solutions, allow the production of N-xylyl-D-methyl
alaninate having formula (V), which is then transformed
15 into the compound having formula (I) operating accord-
ing to what is described in step (b) of the above
process.

Alternatively, (N-phenylacetyl-N-2,6-xylyl)methyl
alaninate having formula (I) can be obtained by conden-
20 sation of methyl pyruvate having formula (X):

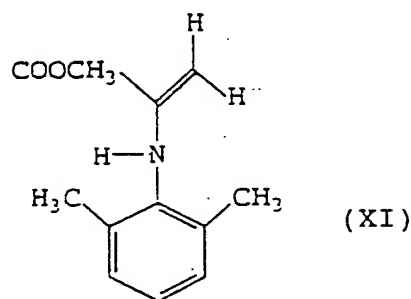


with the xylylidine having formula (IV) described above,
25 in the presence of or without solvents such as, for

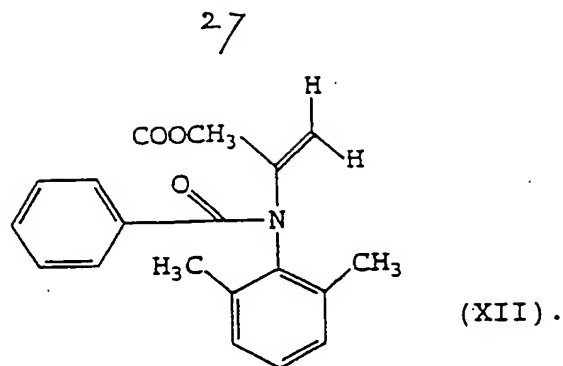
26

example, toluene, ethyl acetate, ethyl alcohol, in the presence of or without dehydrating agents such as, for example, anhydrous sodium sulfate and molecular sieves, operating at a temperature ranging from 20°C to the boiling point of the solution, to obtain the ester N-xylylmethylpropenoate having formula (XI):

10



which is condensed with the chloride of phenylacetic acid, in the presence of or without an organic base such as, for example, triethylamine, N-methyl-morpholine, pyridine, or an inorganic base such as, for example, sodium bicarbonate, in the presence of an organic solvent such as, for example, methylene chloride, ethyl acetate, toluene, xylene, and in the presence of or without a catalyst such as, for example, N,N-dimethylformamide, operating at a temperature ranging from -20°C to the boiling point of the solution, obtaining the ester (N-phenylacetyl-N-2,6-xylyl)-methyl propenoate having formula (XII):



5

The ester (N-phenylacetyl-N-2,6-xylyl)methyl propenoate having formula (XII) is then reduced by catalytic hydrogenation in the presence of a metal such as, for example, ruthenium, palladium, rhodium, platinum, and a chiral inducer such as, for example, a phosphorated derivative such as, for example, 2,2'-bis-(diphenylphosphine)-1,1'-dinaphthyl (known under the trade-name of BINAP) or chiral aminic chelating agents, and in the presence of an alcohol solvent such as, for example, methanol, ethanol, or an organic solvent such as, for example, hexane, cyclohexane, ethyl acetate, toluene, dioxane, or a dipolar aprotic solvent such as, for example, N,N-dimethylformamide, N-methyl-pyrrolidone, operating at a temperature ranging from 20°C to 150°C and at a hydrogen pressure ranging from 1 atm to 30 atms, obtaining N-phenylacetyl-N-xylyl)methyl alaninate having formula (I).

Compound (I) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 148.

Compound (2) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 294.

Compound (3) is described in English patent GB
5 1.500.581.

Compound (4) is described in English patent GB
2.058.059.

Compound (5) is described in "Phytopathological News 12" (1978), Vol. 9, page 142.

10 Compound (6) is described in European patent
application EP 31.257.

Compound (7), also known under the experimental
code of ICIA5504, is described in European patent
application EP 382.375, and its agronomical properties
15 are specified in "Acts of the Brighton Crop Conference"
(1992), pages 435-442.

Compound (8), also known under the experimental
code of BASF490S, is described in European patent
application EP 253.213.

20 Compound (9), also known under the experimental
code of SSF129 and compound (10), also known under the
experimental code of SSF126, are described in Americal
patent US 5.185.242.

Compounds (11)-(15) are described in European
25 patent applications EP 610.764 and EP 550.788.

29

Specific examples of compounds (16), having general formula (VII), which can be used for the purpose of the present invention are:

- manganese ethylenebis(dithiocarbamate) complexed with zinc salts, known as Mancozeb, described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 339;
- manganese ethylenebis(dithiocarbamate), known as Maneb, described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 340;
- zinc ethylenebis(dithiocarbamate), known as Zineb, described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 564.

Compound (17) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 534.

Compound (18) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 469.

Compound (19) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 17.

Compound (20) is described in "The Pesticide

Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 175.

Compound (21) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 537.

Compound (22) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 87.

Compound (23) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 599.

Compound (24) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 120.

Compound (25) is described in European patent application EP 219.756.

Compound (26) is described in European patent applications EP 360.701 and EP 611.232.

Compound (27) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 225.

Compound (28) is described in European patent application EP 234.242.

Compound (29) is described in English patent GB 1.522.657.

31

Compound (30) is described in American patent US 3.912.752.

Compound (31) is described in German patent DE 2.324.010.

5 Compound (32) is described in German patent DE 2.324.010.

Compound (33) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 252.

10 Compound (34) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 422.

Compound (35) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 314.

Compound (36) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 473.

Compound (37) is described in "The Pesticide Manual" (1983), VIIth edition, The British Crop Protection Council Ed., page 461.

Compounds (38) such as, for example, copper oxychloride, copper oxide (I) or (II), copper chloride hydroxide, copper sulfate, can be easily found on the market.

Compound (39) is described in "7th International Congress of Pesticide Chemistry" (1990), Abstract, Hamburg, page 227.

Compound (40) is described in "Brighton Crop
5 Protection Conference - Pests and Diseases" (1996), Atti del Congresso.

Compound (41) is described in European patent application EP 629.616.

Compounds (42) are described in "Pesticide Sci-
10 ence" (1996), Vol. 47, pages 191-197.

Compounds (43) are described in European patent application EP 572.191.

Compounds (44) are described in European patent application EP 753.258.

15 Compounds (45) are described in European patent application EP 652.299.

Compound (46) is described in American patent US 4.931.581.

Preferred fungicidal compositions for the purposes
20 of the present invention are those comprising, as well as the compound having formula (I):

- Mancozeb;
- Mancozeb and Fosetil;
- Mancozeb and Cimoxanil;
- 25 - Fosetil;

- Fosetil and Cimoxanil;
- Propamocarb corresponding to propyl 3-(dimethyl-amino)propylcarbamate;
- Chlorothalonil;
- 5 - a salt of copper (I) or copper (II);
- a salt of copper (I) or copper (II) and Fosetil;
- a salt of copper (I) or copper (II) and Cymoxanil;
- Dimethomorph;
- Flumetover;
- 10 - methylbenzothiadiazole-7-thiocarboxylate;
- one of the following compounds included in the general formula specified in point (43):
- 1-(3-iodine-2-propinyl)-3-(3,5-dichlorophenyl)-5-methylhydantoine;
- 15 1-(3-iodine-2-propinyl)--3--(4-chlorophenyl)-5-methylhydantoine;
- 1-(3-iodine-2-propinyl)--3--(4-fluorophenyl)-5-methylhydantoine;
- 1-(3-iodine-2-propinyl)--3--(3,5-dichlorophenyl)--
- 20 5,5-spiro-cyclopentanhydantoine;
- 1-(3-iodine-2-propinyl)--3--(3,5-dichlorophenyl)--
- 5,5-spiro-cyclohexanhydantoine;
- 1-(3-iodine-2-propinyl)--3--(3,5-dichlorophenyl)--
- 5,5-dimethylhydantoine;
- 25 - one of the following compounds included in the

general formula specified in point (44):

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--
dichloro-4-methylbenzamide;

5 N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--
dichloro-4-ethylbenzamide;

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--
dichloro-4-ethoxybenzamide;

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--
dichloro-4-methoxybenzamide;

10 N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--
dichloro-4-cyanobenzamide;

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--
dibromo-4-methylbenzamide;

- one of the following compounds included in the
15 general formula specified in point (45):

S-R-3-[N-(N-isopropoxycarbonylvalinyl)amino]-3-
isopropyl phenylpropanoate;

S-RS-3-[N-(N-isopropoxycarbonylvalinyl)amino]-3-
isopropyl phenylpropanoate.

20 The fungicidal compositions of the present inven-
tion have a high fungicidal activity with respect to
Oomycetes. Examples of pathogens controlled by the
above compositions, together with examples of applica-
tion crops, are provided below:

25 Plasmopora viticola (vine);

Phytophthora infestans (tomato, potato);

Phytophthora nicotianae (tobacco, ornamental plants, etc.)

Phytophthora palmivora (cacao, etc.)

- 5 Phytophthora cinnamoni (pineapple, cedar, lemon, tomato, etc.)

Phytophthora capsici (pepper, tomato, cucurbitaceae, etc.)

- Phytophthora cryptogea (tomato, thorn-bush, ornamental
10 plants, etc.)

Phytophthora megasperma (ornamental plants, etc.)

Peronospora tabacina (tobacco);

Pseudoperonospora cubensis (cabbage, cucurbitaceae);

Pseudoperonospora humuli (hop);

- 15 Phythium ultimum (various crops); etc.

The fungicidal compositions of the present invention can be prepared by mixing each compound using the following doses per hectare.

- 5-500 g of compound having formula (I);
- 20 - 5-3500 g of each fungicide from (1) to (46).

The fungicidal compositions of the present invention are capable of carrying out a fungicidal activity of both a curative and preventive nature and they also have a limited or no phytotoxicity.

- 25 The above compositions can be applied to any part

36

of the plant, to both the aerial parts (leaves, stems, shoots, branches) and also the hypogeous parts for controlling typical root pathogens, or to the seeds before planting, or even to the earth where the plant
5 grows.

Compositions can be used which are in the form of dry powders, wettable powders, emulsifiable concentrates, microemulsions, pastes, granulates, solutions, suspensions, etc: the selection of the type of composition will depend on its specific use.
10

The compositions are prepared in the known way, for example by diluting or dissolving the active substances with a solvent medium and/or solid diluent, possibly in the presence of surface-active agents.

15 Solid diluents, or carriers, which can be used are: silica, kaolin, bentonite, talc, infusorial earth, dolomite, calcium carbonate, magnesia, chalk, clays, synthetic silicates, attapulgite, sepiolite.

Liquid diluents which can be used, apart from
20 water obviously, are various solvents, for example aromatics (xylols or mixtures of alkylbenzols), chloroaromatics (chlorobenzol), paraffins (petroleum fractions), alcohols (methanol, propanol, butanol, octanol, glycerine), amines, amides (N,N-dimethylformamide, N-methylpyrrolidone), ketones (cyclohexanone, acetone,
25

37

acetophenone, isophorone, ethylamylketone), esters (isobutyl acetate).

Surface-active agents which can be used are salts of sodium, calcium, triethanolamine or triethylamine of
5 alkylsulfonates, alkylarylsulfonates, polyethoxylated alkylphenols, fatty alcohols condensed with ethylene oxide, polyoxyethylated fatty acids, polyoxyethylated sorbitol esters, ligninsulfonates.

The above compositions can also contain special
10 additives for particular purposes such as, for example, adhesion agents, such as wattle gum, polyvinyl alcohol, polyvinylpyrrolidone.

If desired, it is possible to also add other compatible active principles to the compositions of the
15 present invention, such as, for example, other fungicides, phyto regulators, antibiotics, herbicides, insecticides, fertilizers.

Examples of fungicides which can be included in the composition of the invention are alanicarb, amprop-
20 ylfos, azaconazole, azoxystrobin, BAY KTU 3616, benomyl, biloxazol, binapacryl, blastidone S, bromoconazole, bupyrimate, butenaclo, butiobate, captafol, carbendazim, carboxin, quinoethionate, chlorobenzothiazole, chloroneb, clozolinat, clozylacon, copper
25 salts, cyclohexylimide, cyproconazole, cyprofuran, CGA

245 704, diclone diclobutrazole, diclomezine, dicloran,
didecyl- or dimethyl-ammonium chloride, dietofencarb,
difeconazole, dimefluazole, dimethconazole, dimethiri-
mol, diniconazole, dinocap, dipyrithione, ditalimfos,
5 dodemorf, dodine, doguadine, edifenfos, epoxyconazole,
etaconazole, etirimol, ethoxyquin, fenaminosulf,
fenapanil, fenarimol, phenbuconazole, phenfuran,
phenpiclonil, phenpropidine, fenpropimorf, fentin ace-
tate, ferbam, ferimzone, fludioxonyl, fluoroimide,
10 fluotrimazole, flutolanil, flutriafol, fluzilazol,
fuberidazole, furalaxyl, cis-furconazole, guazatine,
ICI A 5504, hydroxyiso-oxazol, imazalil, imibenconazo-
le, ipconazole, iprobenfos, iprodione, isoprotiolane,
kasugamicine, kresoximethyl, mancozeb, maneb, mepronil,
15 metconazole, metfuroxam, metiram, metsulfovax, myclobu-
tanil, neoasozin, nuarimol, oxycarboxyn, perfurazoate,
penconazole, phenazine oxide, phosphoric acids, phthal-
ide, polyoxin D, polyram, probenazole, procloraz,
procimidone, propionic acid, piracarbolid, pyrazofos,
20 pyrimethanyl, pyriphenox, pyroquilon, pyroxyfur,
pyrrolnitrin, compounds containing quaternary ammonium,
quinconazole, quinomethionate, quintozone, rabenazole,
sodium pentachlorophenate, SSF 126, SSF 129, spiroxam-
ine, streptomycine, sulfur, tebuconazole, teclophtha-
25 lam, tecnazene, thiabendazole, ticarbanil, ticiophen,

39

thi fluzamide, 2-(thiocyanomethylthio)benzothiazole,
methyl-thiophanate, timibenconazole, methyl-ticlophos,
triacetate salt of 1,1'-imino-di-(octamethylene)diguani-
idine, triazabutyl, triazaoxide, tricyclazole,
5 tridemorf, triforine, triflumizole, trithiconazole,
validamycine A, vapam, vinclozolin, zineb and ziram.

The concentrations of the active substances in the
above compositions can vary within a wide range,
depending on the crop, pathogen, environmental condi-
10 tions and the type of formulation adopted.

The concentration of the active substances gener-
ally varies from 0.1% to 95%, preferably from 0.5% to
90%.

When the above fungicidal compositions are applied
15 to the leaves, a dose equal to 5-350 g/hl of each
active principle is preferably used for the treatment
of fruit crops whereas a dose equal to 80-3500 g/ha of
each active principle is preferably used for the
treatment of extensive crops (potato, hop, etc.).

20 When the above fungicidal compositions are applied
to the seed, overall doses of active principles equal
to 0.0001-30 g per kilogram of seeds, are used.

The synergetic effect of compound (a) can also be
observed when compounds (a) and (b) are applied sepa-
25 rately to the plant to be treated instead of being

mixed with each other, as occurs in the above compositions in which compound (a) is mixed with one or more fungicides selected from the compounds cited in points 1 to 46. The present invention therefore also relates
5 to a method for controlling phytopathogen fungi in a plant which comprises the application of:

- an effective quantity of compound (a); and
- an effective quantity of one or more fungicides (b);

10 to the seeds, leaves, roots, or earth where the plant grows.

The following examples provide an illustration of the present invention but do not limit its scope. In the examples, the synergetic effect of the components
15 of the mixture can be seen by comparing the experimental data with the theoretical efficiency of the fungicidal composition of the present invention, calculated according to the Limpel formula ("Pesticide Science" (1987), Vol. 19, pages 309-315:

20
$$E = x + y - xy/100$$

wherein:

- E is the fungicidal activity expected, without synergetic effects, from a composition obtained by mixing g.x of compound X with g.y of compound Y;
- 25 - x is the activity of compound X when used alone at

41

the dose g.x;

- y is the activity of compound Y when used alone at the dose g.y.

When the fungicidal activity experimentally
5 obtained, is higher than the value of E, this activity
is considered as being synergetic effect.

EXAMPLE 1

(A₁) Preparation of N-xylyl-D-methyl alaninate.

13.5 g of 2,6-xylylidine (Aldrich) are added to 16.7
10 g of methyl S-bromopropionate obtained by esterifica-
tion of the corresponding Aldrich acid esterified with
methanol under acid conditions, and the mixture is
heated for 3 hours, at a temperature of 110°C. The raw
material obtained is directly purified on silica gel,
15 using a mixture of hexane and ethyl acetate in a ratio
of 7/3 v/v, as eluant.

16.3 g of N-xylyl-D-methyl alaninate are obtained
(yield 79%).

(A₂) Preparation of N-xylyl-D-methyl alaninate.

20 N-xylyl-D-methyl alaninate is also obtained by
operating with an analogous process to that described
above in (A₁) using methyl S-2-tosyloxypropionate or
methyl S-mesyloxypropionate in substitution of methyl
S-bromopropionate, obtaining 82% and 85% yield, respec-
25 tively.

42

(B₁) Preparation of (N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate having formula (II).

A solution of 98 g of N-xylyl-D-methyl alaninate, obtained as described above and 91.4 g of phenylacetic acid chloride in 1200 cm³ of toluene, is heated to reflux temperature, for 2 hours, in the presence of 2.5 cm³ of dimethylformamide.

After cooling, the solution obtained is washed with aqueous bicarbonate and the organic phase is evaporated at reduced pressure after drying with sodium sulfate.

The raw material thus obtained (158 g) is crystallized with abundant hexane obtaining 114 g of a white crystalline solid corresponding to (N-phenylacetyl-N-2,6-xylyl)methyl alaninate with an enantiomeric D/S ratio = 80/20. This white solid is recrystallized three times with a mixture of hexane/ethyl acetate in a ratio 95/5 obtaining decreasing quantities of (N-phenylacetyl-N-2,6-xylyl)methyl alaninate progressively enriched with the desired D isomer:

1st crystallization: 90.0 g (yield of 60%),

D/S ratio = 88/12;

2nd crystallization: 61.4 g (yield of 40%),

D/S ratio = 94/6;

3rd crystallization: 25.8 g (yield of 16.8%),

43

D/S ratio = 98.5/1.5.

The above enantiomeric ratios are determined with a CHIRALCEL OD chiral column (10 μ m - 4.6 x 250 mm), eluating with a mixture of hexane/isopropyl alcohol in a ratio 7/3, at a flow-rate of 0.5 ml/minute.

(B₂) Preparation of (N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate having formula (II).

42 g of sodium bicarbonate are added to a solution of 100 g of N-xylyl-D-methyl alaninate in 500 cm³ of toluene, cooled to a temperature ranging from 5°C to 10°C, and subsequently 75 g of phenylacetic acid chloride are slowly added dropwise.

After 4 hours at room temperature, the above solution is washed with water and then evaporated at reduced pressure after drying with sodium sulfate. The raw material thus obtained is crystallized with abundant hexane obtaining 106 g of a white crystalline solid corresponding to (N-phenylacetyl-N-2,6-xylyl)-methyl alaninate with an enantiomeric D/S ratio = 98/2 (yield 92.5%).

(B₃) Preparation of (N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate having formula (II).

15.5 g of phenylacetic acid chloride are added to a solution of 20.7 g of N-xylyl-D-methyl alaninate, obtained as described above, in 100 cm³ of toluene.

44

After 4 hours at reflux temperature, the reaction is cooled, evaporated at reduced pressure and the raw material obtained is purified on silica gel, using a mixture of hexane and ethyl acetate in a ratio 7/3 v/v, as eluant.

28.9 g of (N-phenylacetyl-N-2,6-xylyl-D-methyl alaninate having formula (II) are obtained, with an $[\alpha]_D$ rotatory optical power of -27.3° ($c = 1$, acetone) (yield 89%).

10 EXAMPLE 2

Analogously to what is described in Example 1, but starting from methyl R-bromopropionate, (N-phenylacetyl-N-2,6-xylyl-D-methyl alaninate having formula (II), is obtained, in two passages, with an $[\alpha]_D$ rotatory optical power of $+27.4^\circ$ ($c = 1$, acetone) (yield 89%).

EXAMPLE 3

Synergetic effects of fungicidal compositions containing (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate and Dimethomorph in the control of infections caused by Plasmopara viticola on vines.

Leaves of cultivar Dolcetto vine plants grown in vases in a conditioned environment ($20 \pm 1^\circ\text{C}$), 70% relative humidity) are treated by spraying both sides with hydroacetic solutions at 20% by volume of acetone of the following compositions (the proportions

of the components are indicated in Table 1):

- (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate (A) and Dimethomorph (B) [indicated above under point (25)];
- 5 - (N-phenyl-acetyl-N-2,6-xylyl)methyl alaninate raceme (C) and Dimethomorph (B) [fungicide indicated under point (25)].

After remaining 24 hours in a conditioned environment, the plants were sprayed on both sides of the
10 leaves with an aqueous suspension of conidia of Plasmo-
pora viticola (200000 conidia per cm³).

The plants were maintained in a humidity saturated environment, at 21°C, for the incubation period of the fungus.

- 15 At the end of this period (7 days), the gravity of the attack is estimated and the defence percentage is calculated according to the following formula:

$$D = (1 - lm_1/lm_0) * 100$$

wherein lm_1 is the disease index of the plants treated
20 and lm_0 is that of the plants not treated (references).

The synergetic effect is obtained from the ratio between the activity experimentally observed and that calculated according to the Limpel formula described above.

- 25 The data obtained are indicated in Table 1.

46

EXAMPLE 4

Synergetic effects of fungicidal compositions containing (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate and S-RS-3-[N-(N-isopropoxycarbonyl-valinyl)amino]isopropyl phenylpropanoate in the control of infections caused by Plasmopara viticola on vines.

Using the same method described in Example 3, the following compositions are tested (the proportions of the components are indicated in Table 2):

- 10 - N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate (A) and S-RS-3-[N-(N-isopropoxycarbonyl-valinyl)-amino]-3-isopropylphenylpropanoate (D) [fungicide included in the general formula indicated above under point (45)].
- 15 - (N-phenyl-acetyl-A-2,6-xylyl)methyl alaninate raceme (C) and S-RS-3-[N-(N-isopropoxycarbonyl-valinyl)amino]-3-isopropylphenylpropanoate (D) [fungicide included in the general formula indicated above under point (45)].

20 The data obtained are indicated in Table 2.

EXAMPLE 5

Synergetic effects of fungicidal compositions containing (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate mixed with the compounds Flumetover (compound 26) and Famoxadone (compound 40) in the control of infections

47

caused by Plasmopara viticola on vines.

Using the same method described in Example 3, the following compositions are tested:

- (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate
5 (A) and Flumetover (E)
- (N-phenyl-acetyl-N-2,6-xylyl)-DL-methyl alaninate
(C) and Flumetover (E)

The data obtained are indicated in table 3.

- (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate
10 (A) and Famoxadone (F)
- (N-phenyl-acetyl-N-2,6-xylyl)-DL-methyl alaninate
(C) and Famoxadone (F)

The data obtained are indicated in table 4.

EXAMPLE 6

- 15 Synergetic effects of fungicidal compositions containing (N-phenyl-acetyl-N-2,6-xylyl)-D-methyl alaninate mixed with Fosetyl Alumino (compound 2) or mixed with Fosetyl Alumino (compound 2) and Mancozeb (compound 16) or mixed with copper hydroxide (compound type 38) in
20 the control of infections caused by Plasmopara viticola on vines.

Three-year old cv. Barbera vines were treated with applications of (N-phenyl-acetyl-N-2,6-xylyl)methyl alaninate mixed with Fosetyl alumino (compound 2) or
25 mixed with Fosetyl alumino (compound 2) and Mancozeb

(compound 16) or mixed with copper hydroxide (compound type 38) at intervals of 12-15 days according to appropriate agronomical practice. In particular a comparison was made of mixtures containing (N-phenyl-
5 acetyl-N-2,6-xylyl)methyl alaninate both in its optically active D form (Compound A) and in its racemic DL form (Compound C). After 3 applications, after observing a significant leaf infection in the reference (72.5%), observation was made of the damage in the
10 parcels treated. The effectiveness was evaluated as control percentage of the disease with respect to the damage observed on the vines which had not been treated, determining the average percentage of damage of 100 leaves. Considering the proven identical activity of a
15 half dose of compound (A) with respect to the full dose of (C), the differences in effectiveness indicated in tables 5-7 can therefore be attributed to the different and greater synergetic effect shown by form D (Compound A) mixed with the partners used.

49

TABLE 1

	(A) or (C) concentration	Concentration of (B) (ppm)	Limpel expected activity (%)	Activity observed	Activ.obser./ activ.calcul.
(C)	0.20	--	--	35.0	--
(A)	0.10	--	--	36.0	--
-	--	0.40	--	30.0	--
(C)	0.20	0.40	54.5	59.5	1.10
(A)	0.10	0.40	55.0	69.0	1.25

TABLE 2

	(A) or (C) concentration	Concentration of (D) (ppm)	Limpel expected activity (%)	Activity observed	Activ.obser./ activ.calcul.
(C)	0.20	--	--	35.0	--
(A)	0.10	--	--	38.0	--
-	--	1.80	--	15.0	--
(C)	0.20	0.40	45.0	52.0	1.15
(A)	0.10	0.40	45.5	61.0	1.35

TABLE 3

	(A) or (C) concentration	Concentration of (E) (ppm)	Limpel expected activity (%)	Activity observed	Activ.obser./ activ.calcul.
(C)	0.20	--	--	35.0	--
(A)	0.10	--	--	36.0	--
-	--	0.15	--	28.0	--
(C)	0.20	0.15	53.2	60.1	1.13
(A)	0.10	0.15	53.9	69.5	1.29

TABLE 4

	(A) or (C) concentration	Concentration of (F) (ppm)	Limpel expected activity (%)	Activity observed	Activ.obser./ activ.calcul.
(C)	0.20	--	--	35.0	--
(A)	0.10	--	--	36.0	--
-	--	0.10	--	20.0	--
(C)	0.20	0.10	48.0	56.6	1.13
(A)	0.10	0.10	48.8	63.9	1.31

TABLE 5

Activity of mixtures of (N-phenyl-acetyl-N-2,6-xylyl)methyl alaninate with Fosetyl Aluminum (compound 2)				
Product	(A) or (C) concentration (g/hl)	Product (2) concentration (g/hl)	Activity observed	
(A)	10	160	99.9	
(C)	20	160	97.5	

TABLE 6

Activity of mixtures of (N-phenyl-acetyl-N-2,6-xylyl)methyl alaninate with Fosetyl Aluminum (compound 2) and Mancozeb (compound 16)				
Product	(A) or (C) concentration (g/hl)	Products (2) and (16) concentrations (g/hl)	Activity observed	
(A)	5	140+140	99.9	
(C)	10	140+140	98.2	

TABLE 7

Activity of mixtures of (N-phenyl-acetyl-N-2,6-xylyl)methyl alaninate with copper hydroxide (compound like 38)				
Product	(A) or (C) concentration (g/hl)	Product (2) concentration (g/hl)	Activity observed	
(A)	10	100	99.2	
(C)	20	100	98.6	

EXAMPLE 7

Activity "in vitro" on Phythium ultimum.

(N-phenylacetyl-N-2,6-xylyl)-D-methyl alaninate having formula (II) obtained as described above, (N-phenylacetyl-N-2,6-xylyl)-L-methyl alaninate and (N-phenylacetyl-N-2,6-xylyl)-DL-methyl alaninate (Benalaxyl) are incorporated in an agarized culture medium, at a temperature of 50°C, which is distributed into Petri capsules with a diameter of 55 mm. After solidification of the agarized medium, the capsules are inoculated by placing in the centre a disk having a diameter of 6 mm of of agar supporting the mycelium of the fungus under examination (Phythium ultimum).

After 5 days of conservation at 28°C, the diameter of the colony which has developed is measured and is related to the diameter of a colony cultivated on non-treated medium.

On the basis of these measurements the percentage of growth inhibition is calculated according to the formula:

$$I = (1 - d_1/d_0) * 100$$

wherein d_1 is the diameter of the treated colony and d_0 that of the non-treated colony.

The above laevorotatory (D), dextrorotatory (L) and racemic (DL) compounds are tested at different

concentrations to establish the minimum quantity capable of inhibiting 50% of myceliary growth (MIC). The data obtained are indicated in Table 8.

TABLE 8

5	=====	
	FORM	MIC
		(ppm)
	D	0.05
	DL	0.20
10	L	40.00
	=====	

EXAMPLE 8

Determination of the residues of active principle in hops.

15 Small hop plants are treated with six leaf applications of (N-pehnylacetyl-N-2,6-xylyl-D-methyl alaninate having formula (II) obtained as described above, or N-phenylacetyl-N-2,6-xylyl-DL-methyl alaninate (Benalaxyl), at a dose of 450 g/ha, at intervals of 10-15
20 days.

Samples of hops, equal to about 1 kg of humid vegetable, are removed after carrying out the last treatment (T_0) and subsequently after 1 day (T_1) and after three days (T_3).

25 Each sample is homogenized and ground with ace-

tone. The suspension obtained is then filtered on glass fibre (GF/C W Whatman) under vacuum. The liquid phase is evaporated and the aqueous residue obtained is extracted with methylene chloride.

5 The organic phase is concentrated and the organic extract thus obtained is purified on alumina, eluting with hexane/acetone in a ratio 90/10. The fractions containing the active principle are collected, which are subsequently evaporated and ethylene acetate is
10 added up to a known volume. The content of active principle is then determined by means of gas-chromatographic analysis (GLC/FID; "alkaline flame ionization detector) with respect to an external standard and referring to the original sample.

15 The averages of the data obtained are indicated in Table 9 wherein (D) indicates the laevorotatory compound and (DL) indicates the raceme.

TABLE 9

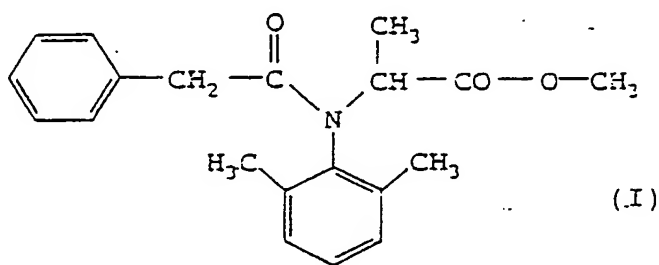
=====			
RESIDUES OF ACTIVE PRINCIPLE (D) OR (DL) IN			
SAMPLES OF HOPS			
(mg/kg)			
5	DAY OF COLLECTION	RESIDUE OF	RESIDUE OF
	OF SAMPLE	COMPOUND (DL)	COMPOUND (D)
	T ₀	3.070	2.990
	T ₁	2.717	2.513
10	T ₂	1.358	0.980
=====			

56

CLAIMS

1. Fungicidal compositions comprising:

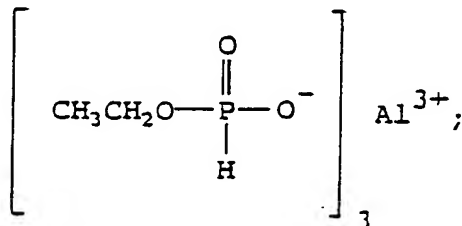
- (a) the compound corresponding to (N-phenylacetyl-N-2,6-xylyl)methyl alaninate having formula (I):



wherein more than 50% of said compound having formula (I) consists of the laevorotatory enantiomorph;

(b) one or more fungicides selected from:

- (1) Cymoxanil corresponding to 1-(2-cyano-2-methoxyiminoacetyl)-3-ethyl-urea;
- (2) Fosetyl having the formula:



- (3) Metalaxyl corresponding to methyl-N-(2-methoxyacetyl)-N-2,6-xylyl-DL-alaninate;
- (4) Oxadixyl corresponding to 2-methoxy-N-(2-oxo-1,3-oxazolidin-3-yl)--acet-2'-6'-

57

-xylidine;

- (5) Ofurace corresponding to DL-3-[N-chloro-acetyl-N-(2,6-dimethylphenyl)-amino]- γ -butyrolactone;
- 5 (6) Fluazinam corresponding to 3-chloro-N-[3-chloro--2,6-dinitro-4--(trifluoromethyl)-phenyl]-5-trifluoromethyl-2-pyridinamine;
- 10 (7) (E)-2-[2-([6--(2-cyanophenoxy)--pyrimidin-4-yloxy]-phenyl-3-methyl methoxyacrylate;
- (8) (E)-methoxyimino- α -o-tolyloxy)-o-tolyl]-methyl acetate;
- 15 (9) N-methyl-(E)-methoxyimino-[2-(2,5-dimethyl-phenoxy-methyl)-phenyl] acetamide;
- (10) N-methyl-(E)-methoxyimino-[2-phenoxyphenyl]acetamide;
- (11) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-chloro-phenyl)-ethyl]-amino]-carbonyl]-propyl]-carbamate;
- 20 (12) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-methyl-phenyl)-ethyl]-amino]-carbonyl]-propyl]-carbamate;
- (13) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-ethyl-phenyl)-ethyl]-amino]-carbonyl]-
- 25

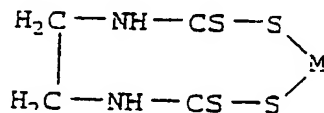
58

propyl]-carbamate;

(14) O-(1-methylethyl)-N-[2-methyl-1-[[[1-(4-methoxyphenyl)-ethyl]-amino]-carbonyl]--propyl]--carbamate;

5 (15) O-(phenyl)--N--[2-methyl-1-[[[1-(4-methoxyphenyl)-ethyl]-amino]-carbonyl]--propyl]--carbamate;

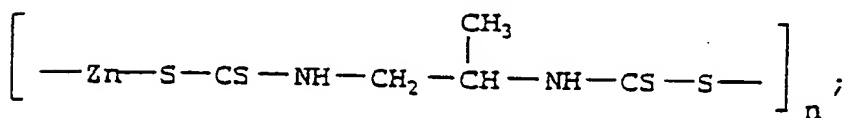
(16) compounds belonging to the group of dithiocarbamates having the general
10 formula:



wherein M represents manganese or zinc;

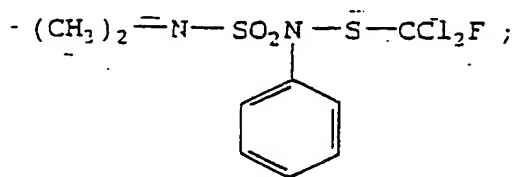
15 (17) Thiram corresponding to bis-(dimethylthiocarbamoyl)-disulfide;

(18) Propineb having the formula:



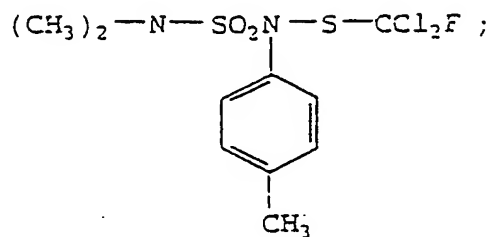
20 (19) Anilazine corresponding to N-(4,6-dichloro-1,3,5-triazin-2-yl)-aniline;

(20) Dichlofluanid having the formula:



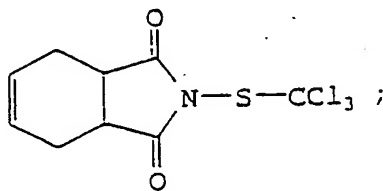
59

(21) Tolyfluanid having the formula:



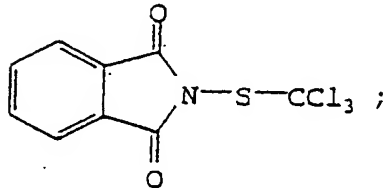
5

(22) Captan having the formula:



10

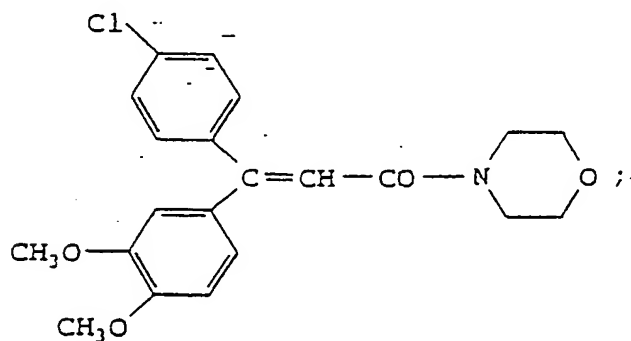
(23) Folpet having the formula:



15

(24) Chlorothalonil corresponding to 1,3-dicyano-2,4,5,6-tetrachlorobenzene;

(25) Dimethomorph having the formula:



20

25

(26) Flumetover corresponding to N,N-diethyl-

60

amide of 4-trifluoromethyl-6-(3,4-dimethoxyphenyl)-benzoic acid;

5 (27) Dithianon corresponding to 5,10-dihydro-5,10-dioxonaphthol-[2,3-b]-1,4-dithin-2,3-dicarbonitrile;

(28) Tetraconazole corresponding to 1-(1H-1,2,4-triazol-1-yl)-2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy)-propane;

10 (29) Propiconazole corresponding to 1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole;

(30) Triadimefon corresponding to 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butanone;

15

(31) Triadimenol corresponding to 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-ol;

(32) Bitertanol corresponding to 1-(diphenyl-4-yloxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-ol;

20

(33) Etridiazole corresponding to ethyl 3-trichloromethyl-1,2,4-thiadiazolyl ether;

25 (34) Pencycuron corresponding to 1-(4-chloro-

61

benzyl)-1-cyclopentyl-3-phenylurea;

(35) Hymexanol corresponding to 5-methylisoxazol-3-ol;

(36) Protiocarb corresponding to S-ethyl-(3-dimethylaminopropyl)-thiocarbamate;

(37) Propamocarb corresponding to propyl 3-(dimethylamino)-propylcarbamate;

(38) salts of copper (I) or copper (II);

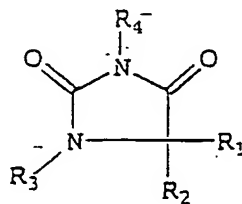
(39) Andoprim corresponding to 2-p-methoxyaniline-4,6-dimethyl-pyrimidine;

(40) Famoxadone or DPX-JE874 corresponding to 5-methyl-5-(4-phenoxyphenyl)-3-(phenylamino)-oxazolidin-2,4-dione;

(41) 4-methyl-4-phenyl-1-(phenylamino)-2-methylthio-imidazolidin-5-one;

(42) pyrimidinic compounds such as, for example, cyprodinil, mepanipyrim, pyrethanil;

(43) compounds having the following general formula:



wherein:

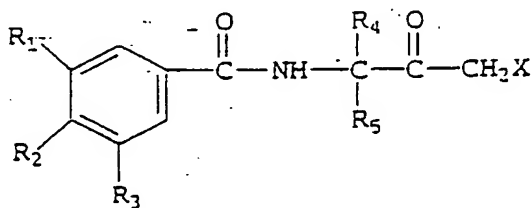
- R₁ and R₂, the same or different, repre-

62

sent a hydrogen atom; or a C₁-C₃ alkyl group; or, R₁ and R₂ together with the hydantoinic ring to which they are attached, represent a C₃-C₇ saturated spiro ring;

- R₃ and R₄, different from each other, represent a C₁-C₃ alkyl group; a phenyl group, said phenyl group optionally substituted with a halogen atom, with a nitro group, with a C₁-C₃ alkoxy group, or with a C₁-C₃ haloalkyl group; or a 3-iodo-propinyl group;

(44) compounds having the following general formula:



wherein:

- R₁ and R₃, the same or different, represent a halogen atom; or a C₁-C₄ alkyl group;
- R₂ represents a C₁-C₄ alkyl group; a C₂-C₄ alkenyl group; a C₂-C₆ alkynyl group; a C₁-C₄ alkoxy group; a cyano group;

63

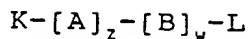
- R_4 and R_5 , the same or different, represent a halogen atom; or a C_1 - C_4 alkyl group; on the condition that, at least one between R_4 and R_5 , is a C_2 - C_4 alkyl group;

5

- X represents a halogen atom; a thiocyano group; an isothiocyano group;

(45) oligopeptidic compounds having the general formula:

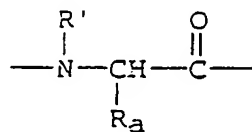
10



wherein:

- z and w, the same or different, are 1 or 2;
- A represents an aminoacidic portion having the general formula:

15



wherein:

20

- R_a represents a linear or branched C_3 - C_4 alkyl group; or a C_3 - C_4 cycloalkyl group;
- R' represents a hydrogen atom; a C_1 - C_3 alkyl group; or, together with R_a it forms a linear or branched C_3 - C_5 alkyl-

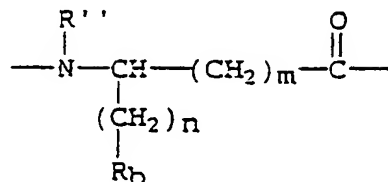
25

64

ene chain;

- B represents an aminoacid portion having the general formula:

5

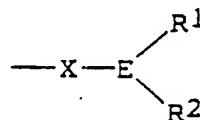


wherein:

10

- R_b represents a phenyl group or an aromatic heterocyclic group, said phenyl and heterocyclic groups, also optionally substituted;
- m and n, the same or different, are 0 or 1;
- R'' represents a hydrogen atom; or a $\text{C}_1\text{-C}_3$ alkyl group;
- L represents a group having the general formula:

15



20

wherein:

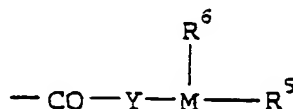
- E represents a linear or branched $\text{C}_1\text{-C}_8$ alkylene chain; a linear or branched $\text{C}_2\text{-C}_8$ ω -oxalkyl chain; or a direct bond;
- R^1 represents a hydrogen atom; a $\text{C}_3\text{-C}_6$

25

65

cycloalkyl group; a phenyl group or an aromatic heterocyclic group, said phenyl and heterocyclic groups also optionally substituted;

- 5 - R^2 represents a hydrogen atom; a linear or branched C_2-C_6 carboxyalkyl group; a linear, branched or cyclic C_2-C_6 carbamoyl group; or a cyano group;
- 10 - X represents an -O- group; an $-N(R^3)-$ group; or an $-N(R^4)-O-$ group; wherein:
- 15 - R^3 represents a hydrogen atom; a C_1-C_3 alkyl or alkoxyl group; or, together with R_1 , it represents a direct bond or a linear or branched C_2-C_4 alkylene chain;
- R^4 represents a hydrogen atom; a C_1-C_3 alkyl group; or, together with R_1 , it represents a direct bond;
- 20 - K represents a hydrogen atom; a linear or branched C_1-C_4 alkyl group; or a protective group having general formula:



25

wherein:

66

- 5
- Y represents an oxygen atom; or a direct bond;
 - M represents a linear, branched or cyclic C₁-C₈ alkylene chain; or a direct bond;
 - R⁵ represents a hydrogen atom; a phenyl group optionally substituted; a linear, branched or cyclic C₂-C₆ carbamoyl group; a linear, branched or cyclic C₁-C₆ carboalkoxy group; or a cyano group;
 - R⁶ represents a hydrogen atom; a C₁-C₃ alkoxy group; an acetate group; or an acetamidic group;
- 10
- 15 (46) methylbenzothiadiazole-7-thiocarboxylate.
2. The fungicidal compositions according to claim 1, wherein the compound having formula (I) contains more than 90% of laevorotatory enantiomorph.
- 20 3. The fungicidal compositions according to claim 1, wherein the compound having formula (I) contains more than 95% of laevorotatory enantiomorph.
4. The fungicidal compositions according to claim 1, wherein the compound having formula (I) contains
- 25 more than 99% of laevorotatory enantiomorph.

67

5. The fungicidal compositions according to claim 1,
wherein the fungicide (b) is Mancozeb.
6. The fungicidal compositions according to claim 1,
wherein the fungicides (b) are Mancozeb and
5 Fosetil.
7. The fungicidal compositions according to claim 1,
wherein the fungicides (b) are Mancozeb and
Cimoxanil.
8. The fungicidal compositions according to claim 1,
10 wherein the fungicide (b) is Fosetil.
9. The fungicidal compositions according to claim 1,
wherein the fungicides (b) are Fosetil and Cimoxa-
nil.
10. The fungicidal compositions according to claim 1,
15 wherein the fungicide (b) is Propamocarb corre-
sponding to propyl 3-(dimethylamino)-propylcarbam-
ate.
11. The fungicidal compositions according to claim 1,
wherein the fungicide (b) is Chlorothalonil.
- 20 12. The fungicidal compositions according to claim 1,
wherein the fungicide (b) is a salt of copper (I)
or copper (II).
13. The fungicidal compositions according to claim 1,
wherein the fungicides (b) are a salt of copper
25 (I) or copper (II) and Fosetil.

60

14. The fungicidal compositions according to claim 1,
wherein the fungicides (b) are a salt of copper
(I) or copper (II) and Cymoxanil.
15. The fungicidal compositions according to claim 1,
5 wherein the fungicide (b) is Dimethomorph.
16. The fungicidal compositions according to claim 1,
wherein the fungicide (b) is Flumetover.
17. The fungicidal compositions according to claim 1,
wherein the fungicide (b) is methylbenzothiadiaz-
10 ole-7-thiocarboxylate.
18. The fungicidal compositions according to claim 1,
wherein the fungicide (b) is one of the following
compounds included in the general formula speci-
fied under point (43):
- 15 1-(3-iodine-2-propinyl)-3-(3,5-dichlorophenyl)-5-
methylhydantoin;
- 1-(3-iodine-2-propinyl)--3--(4-chlorophenyl)-5-
methylhydantoin;
- 1-(3-iodine-2-propinyl)--3--(4-fluorophenyl)-5-
20 methylhydantoin;
- 1-(3-iodine-2-propinyl)--3--(3,5-dichlorophenyl)--
5,5-spiro-cyclopentanhydantoin;
- 1-(3-iodine-2-propinyl)--3--(3,5-dichlorophenyl)--
5,5-spiro-cyclohexanhydantoin;
- 25 1-(3-iodine-2-propinyl)--3--(3,5-dichlorophenyl)--

69

5,5-dimethylhydantoin;

19. The fungicidal compositions according to claim 1, wherein the fungicide (b) is one of the following compounds included in the general formula specified under point (44):

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--dichloro-4-methylbenzamide;

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--dichloro-4-ethylbenzamide;

10 N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--dichloro-4-ethoxybenzamide;

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--dichloro-4-methoxybenzamide;

15 N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--dichloro-4-cyanobenzamide;

N-[3'-(1'-chloro-3'-methyl-2'-oxopentane)]--3,5--dibromo-4-methylbenzamide.

20. The fungicidal compositions according to claim 1, wherein the fungicide (b) is one of the following compounds included in the general formula specified under point (45):

S-R-3-[N-(N-isopropoxycarbonylvalinyl)amino]-3-isopropyl phenylpropanoate;

25 S-RS-3-[N-(N-isopropoxycarbonylvalinyl)amino]-3-isopropyl phenylpropanoate.

70

- DOCID: <W0 9826654A2 1 >

71

hypogeous parts for controlling typical root pathogens, or to the seeds before planting, or to the earth where the plant grows.

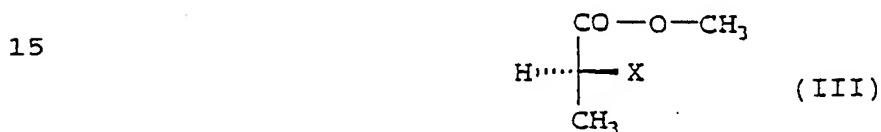
26. A method for controlling phytopathogen fungi in a plant which comprises applying:

- an effective quantity of compound (a); and
- an effective quantity of one or more fungicides (b);

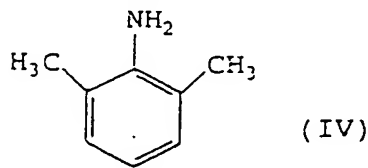
to the seeds, leaves, roots, or to the earth where the plant grows.

27. A process for the preparation of the compound having formula (I) comprising:

(a) reacting methyl ester having general formula (III):

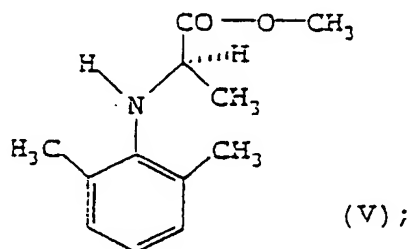


having an S-type asymmetrical carbon and wherein X represents a halogen atom; or X represents an activated ester such as a paratoluenesulfonate, a mesilate or triflate; with an xylidine having formula (IV):



72

in the presence of or without an inert organic solvent or a mixture of inert organic solvents, at a temperature ranging from 60°C to the boiling point of the solvent system selected, in the presence of or without an organic or inorganic base, obtaining N-xylyl-D-methyl alaninate having formula (V):



- (b) acylating the N-xylyl-D-methyl alaninate having formula (V) obtained in step (a), with a derivative of phenylacetic acid; or with a mixed anhydride obtained by reaction of the salt of phenylacetic acid with an acyl chloride; or with an alkyl chloroformate; in the presence of an aromatic solvent or a halogenated solvent, or an ester solvent, at a temperature ranging from -20°C to + 40°C, in the presence of an organic or inorganic base.
28. The process according to claim 27, wherein in step (b) the aromatic solvent is toluene.
29. The process according to claim 27, wherein in step

73

(b) the halogenated solvent is dichloromethane or dichloroethane.

30. The process according to claim 27, wherein in step (b) the ester solvent is ethyl acetate.

5 31. The process according to claim 27, wherein in step (b) the inorganic base is sodium bicarbonate.

32. The process according to claim 27, wherein in step (b) the organic base is triethylamine or pyridine.

10 33. The process according to any of the previous claims from 27 to 32, wherein in step (b) the temperature is between -5°C and $+ 25^{\circ}\text{C}$.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 37/46, C07C 227/06	A3	(11) International Publication Number: WO 98/26654 (43) International Publication Date: 25 June 1998 (25.06.98)
---	-----------	---

(21) International Application Number: PCT/EP97/06968

(22) International Filing Date: 6 December 1997 (06.12.97)

(30) Priority Data:

MI96A002660	19 December 1996 (19.12.96)	IT
MI97A001198	22 May 1997 (22.05.97)	IT

(71) Applicant (for all designated States except US): ISAGRO S.P.A. [IT/IT]; Via Felice Casati, 20, I-20124 Milano (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): PALLA, Ottorino [IT/IT]; Via Goldoni, 7, I-26013 Crema (IT). MIRENNA, Luigi [IT/IT]; Via Gamboloita, 4, I-20139 Milano (IT). COLOMBO, Laura [IT/IT]; Via Bocconi, 60, I-20090 Lodi (IT). ZINI, Guido [IT/IT]; Viale Giulio Cesare, 24, I-28100 Novara (IT). FILIPPINI, Lucio [IT/IT]; Via Morandi, 13/A, I-20097 San Donato Milanese (IT). ZANARDI, Giampaolo [IT/IT]; Viale Roma, 19, I-28100 Novara (IT).

(74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanò & Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121 Milano (IT).

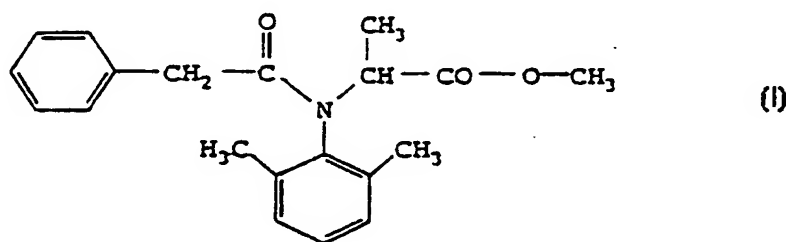
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(88) Date of publication of the international search report:
22 October 1998 (22.10.98)

(54) Title: FUNGICIDAL COMPOSITIONS BASED ON (N-PHENYLACETYL-N-2,6-XYLYL)METHYL ALANINATE



(57) Abstract

Fungicidal compositions comprising: (a) the compound corresponding to (N-phenylacetyl-N-xylyl)methyl alaninate having formula (I), wherein more than 50 % of the compound with formula (I) consists of the laevorotatory enantiomorph; (b) one or more known fungicides. Among known fungicides, Mancozeb, Fosetil, Cymoxanil, Propamocarb, Chlorothalonil, salts of copper (I) or copper (II), etc., can be mentioned. The above compositions can be used in the agricultural field for controlling fungine diseases which seriously damage agricultural crops.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/06968

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N37/46 C07C227/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 01560 A (CIBA GEIGY) 25 January 1996 * see the whole document* ---	1-26
A	WO 96 01559 A (CIBA GEIGY) 25 January 1996 ---	
A	GOZZO ET AL.: "Recent progress in the field of N-Acylalanines as systemic fungicides" PESTICIDE SCIENCE, vol. 16, 1985, pages 277-286, XP002064239 cited in the application -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

7 May 1998

Date of mailing of the international search report

07.09.98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fort, M

INTERNATIONAL SEARCH REPORT

Inter. application No.
PCT/EP 97/06968

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-26

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-26

Fungicidal composition comprising:

(a) the compound corresponding to
(N-phenylacetyl-N-2,6-xylyl)methyl alaninate having formula
(I) wherein more than 50% of said compound consists of the
laevorotatory enantiomer

and

(b) one or more fungicides selected from the compounds (1)
to (46) as defined in claim 1

2. Claims: 27-33

A process for the preparation of the compound of formula (I)
wherein more than 50% of said compound having formula (I)
consists of the laevorotatory enantiomer.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/06968

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9601560 A	25-01-1996	CH 687169 A	15-10-1996
		US 5648383 A	15-07-1997
		AU 2926095 A	09-02-1996
		BG 101192 A	29-08-1997
		BR 9508379 A	23-12-1997
		CA 2194175 A	25-01-1996
		CN 1152253 A	18-06-1997
		CZ 9700061 A	16-04-1997
		EP 0769901 A	02-05-1997
		FI 970080 A	08-01-1997
		HU 76690 A	28-10-1997
		JP 10502380 T	03-03-1998
		NO 970091 A	07-03-1997
		PL 318146 A	12-05-1997
		SK 2597 A	10-09-1997
		ZA 9505709 A	11-01-1996

WO 9601559 A	25-01-1996	CH 686856 A	31-07-1996
		AU 2925995 A	09-02-1996
		BG 101141 A	29-08-1997
		BR 9508381 A	23-12-1997
		CA 2194581 A	25-01-1996
		CN 1152252 A	18-06-1997
		CZ 9700060 A	16-04-1997
		DE 29511079 U	14-12-1995
		EP 0769900 A	02-05-1997
		FI 970079 A	08-01-1997
		HU 75809 A	28-05-1997
		JP 10502379 T	03-03-1998
		NO 970090 A	28-02-1997
		PL 318018 A	12-05-1997
		SK 2497 A	09-07-1997
		US 5723491 A	03-03-1998
		ZA 9505708 A	16-01-1996
		HR 950369 A	31-08-1997



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 37/46, C07C 227/06	A3	(11) International Publication Number: WO 98/26654
		(43) International Publication Date: 25 June 1998 (25.06.98)

(21) International Application Number: PCT/EP97/06968

(22) International Filing Date: 6 December 1997 (06.12.97)

(30) Priority Data:

MI96A002660	19 December 1996 (19.12.96)	IT
MI97A001198	22 May 1997 (22.05.97)	IT

(71) Applicant (for all designated States except US): ISAGRO S.P.A. [IT/IT]; Via Felice Casati, 20, I-20124 Milano (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): PALLA, Ottorino [IT/IT]; Via Goldoni, 7, I-26013 Crema (IT). MIRENNA, Luigi [IT/IT]; Via Gamboloita, 4, I-20139 Milano (IT). COLOMBO, Laura [IT/IT]; Via Bocconi, 60, I-20090 Lodi (IT). ZINI, Guido [IT/IT]; Viale Giulio Cesare, 24, I-28100 Novara (IT). FILIPPINI, Lucio [IT/IT]; Via Morandi, 13/A, I-20097 San Donato Milanese (IT). ZANARDI, Giampaolo [IT/IT]; Viale Roma, 19, I-28100 Novara (IT).

(74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanò & Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121 Milano (IT).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

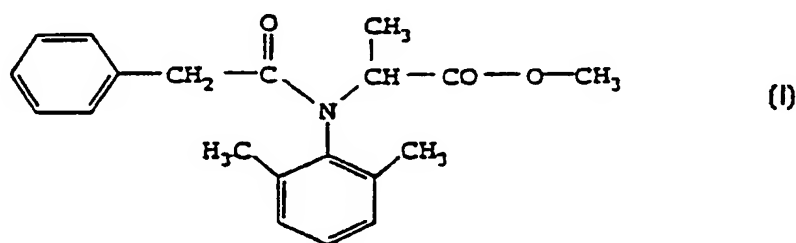
Published

*With a revised version of the international search report.
Before the expiration of the time limit for amending the claims
and to be republished in the event of the receipt of amendments.*

(88) Date of publication of the international search report:
22 October 1998 (22.10.98)

(88) Date of publication of the revised version of the international search report:
26 November 1998 (26.11.98)

(54) Title: FUNGICIDAL COMPOSITIONS BASED ON (N-PHENYLACETYL-N-2,6-XYLYL)METHYL ALANINATE



(57) Abstract

Fungicidal compositions comprising: (a) the compound corresponding to (N-phenylacetyl-N-xylyl)methyl alaninate having formula (I), wherein more than 50 % of the compound with formula (I) consists of the laevorotatory enantiomorph; (b) one or more known fungicides. Among known fungicides, Mancozeb, Fosetil, Cymoxanil, Propamocarb, Chlorothalonil, salts of copper (I) or copper (II), etc., can be mentioned. The above compositions can be used in the agricultural field for controlling fungine diseases which seriously damage agricultural crops.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

REVISED
VERSION

INTERNATIONAL SEARCH REPORT

In Application No
PCT/EP 97/06968

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N37/46 C07C227/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 01560 A (CIBA GEIGY) 25 January 1996 * see the whole document*	1-26
X	GOZZO ET AL.: "Recent progress in the field of N-Acylalanines as systemic fungicides" PESTICIDE SCIENCE, vol. 16, 1985, pages 277-286, XP002064239 cited in the application * see p.279, 2.1.1. Enantiomers of benalaxyl*	27-33
A	WO 96 01559 A (CIBA EIGY) 25 January 1996	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 October 1998

Date of mailing of the international search report

15.10.1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fort, M

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 97/06968

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-26

Fungicidal composition comprising:

(a) the compound corresponding to
(N-phenylacetyl-N-2,6-xylyl)methyl alaninate having formula
(I) wherein more than 50% of said compound consists of the
laevorotatory enantiomer

and

(b) one or more fungicides selected from the compounds (1)
to (46) as defined in claim 1

2. Claims: 27-33

A process for the preparation of the compound of formula (I)
wherein more than 50% of said compound having formula (I)
consists of the laevorotatory enantiomer.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/06968

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9601560 A	25-01-1996	CH 687169 A	15-10-1996
		US 5648383 A	15-07-1997
		AU 2926095 A	09-02-1996
		BG 101192 A	29-08-1997
		BR 9508379 A	23-12-1997
		CA 2194175 A	25-01-1996
		CN 1152253 A	18-06-1997
		CZ 9700061 A	16-04-1997
		EP 0769901 A	02-05-1997
		FI 970080 A	08-01-1997
		HU 76690 A	28-10-1997
		JP 10502380 T	03-03-1998
		NO 970091 A	07-03-1997
		PL 318146 A	12-05-1997
		SK 2597 A	10-09-1997
		ZA 9505709 A	11-01-1996
WO 9601559 A	25-01-1996	CH 686856 A	31-07-1996
		AU 2925995 A	09-02-1996
		BG 101141 A	29-08-1997
		BR 9508381 A	23-12-1997
		CA 2194581 A	25-01-1996
		CN 1152252 A	18-06-1997
		CZ 9700060 A	16-04-1997
		DE 29511079 U	14-12-1995
		EP 0769900 A	02-05-1997
		FI 970079 A	08-01-1997
		HU 75809 A	28-05-1997
		JP 10502379 T	03-03-1998
		NO 970090 A	28-02-1997
		PL 318018 A	12-05-1997
		SK 2497 A	09-07-1997
		US 5723491 A	03-03-1998
		ZA 9505708 A	16-01-1996
		HR 950369 A	31-08-1997